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(21)Application number : **11-103357**(71)Applicant : **SUMITOMO METAL IND LTD**(22)Date of filing : **09.04.1999**(72)Inventor : **TARUYA YOSHIO
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(54) SOLID HIGH POLYMER FUEL CELL**(57)Abstract:**

PROBLEM TO BE SOLVED: To extremely reduce poisoning of respective electrode carrying catalysts by an eluting metallic ion by constituting a separator of S, P, V, Ni, Cu, Cr, Mo having the specific composition and ferrite stainless steel including a rare earth element.

SOLUTION: Ferrite stainless steel for constituting a separator has the following composition. Respective component elements of S not more than 0.005%, P not more than 0.025%, V not more than 0.2%, Ni not more than 0.2%, Cu not more than 0.2%, Cr of 10.5 to 35%, Mo of 0 to 6% and a rare earth element of 0 to 0.1% are included in wt.%, and Cr+3Mo falls within a range of 10.5 to 43%. The stainless steel can include Si not more than 0.3%, Mn not more than 0.4%, C and N not more than 0.018% respectively and C+N%≤0.025%. Ti not more than 0.2%, (6 to 25)×(C%+N%), Nb not more than 0.3% and (6 to 25)×C% can be included when necessary.

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(54)【発明の名称】 固体高分子型燃料電池

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(57)【特許請求の範囲】

【請求項1】固体高分子電解質膜を中央にして燃料電極膜と酸化剤電極膜を重ね合わせた単位電池を複数個、単位電池間にセパレータを介在させて積層した積層体に、*

S:0.005%以下、

V:0.2%以下、

Cu:0.2%以下、

Mo:0~6%、

を含有し、かつ(Cr+3Mo)が10.5~43%の範囲内にある

【請求項2】フェライト系ステンレス鋼中のSiおよびMnが、重量%で、Si量が0.3%以下、Mnが0.4%以下であることを特徴とする請求項1記載の固体高分子型燃料電池。

【請求項3】

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*燃料ガスと酸化剤ガスを供給して直流電力を発生させる固体高分子型燃料電池において、セパレータが下記の化学組成を有するフェライト系ステンレス鋼からなることを特徴とする固体高分子型燃料電池。重量%で、

P:0.025%以下、

Ni:0.2%以下、

Cr:10.5~35%、

希土類元素:0~0.1%

※ライト系ステンレス鋼中のCおよびN量が、重量%で、
10 C:0.018%以下、N:0.018%以下、かつCとNの合計含有量が、0.025%以下である請求項1または2記載の固体高分子型燃料電池。

【請求項4】フェライト系ステンレス鋼が、TiとNbの1種または2種を含有しており、Tiが、重量%で0.2%以下で、かつ6(C%+N%)~25(C%+

N%)の範囲、およびNbが0.3%以下で、かつ6C%~25C%の範囲内にある請求項1から3のいずれか記載の固体高分子型燃料電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、自動車搭載用や家庭用等の小型分散型電源として用いられる固体高分子型燃料電池に関する。

【0002】

【従来の技術】燃料電池は、水素および酸素を利用して直流電力を発電する電池であり、固体電解質型燃料電池、熔融炭酸塩型燃料電池、リン酸型燃料電池および固体高分子型燃料電池などがある。燃料電池の名称は、電池の根幹をなす『電解質』部分の構成材料に由来している。

【0003】現在、商用段階に達している燃料電池には、リン酸型燃料電池、熔融炭酸塩型燃料電池がある。燃料電池のおおよその運転温度は、固体電解質型燃料電池で1000℃、熔融炭酸塩型燃料電池で650℃、リン酸型燃料電池で200℃および固体高分子型燃料電池で80℃である。

【0004】固体電解質型燃料電池は、運転温度が80℃前後と低く起動-停止が容易であり、エネルギー効率も40%程度が期待できることから、小事業所、電話局などの非常用分散電源、都市ガスを燃料とする家庭用小型分散電源、水素ガス、メタノールあるいはガソリンを燃料とする低公害電気自動車搭載用電源として、世界的に実用化が期待されている。

【0005】上記の各種の燃料電池は、『燃料電池』と言う共通の呼称で呼ばれているものの、それぞれの電池構成材料を考える場合には、全く別物として捉えることが必要である。使用される電解質による構成材料の腐食の有無、380℃付近から顕在化し始める高温酸化の有無、電解質の昇華と再析出、凝結の有無等により求められる性能、特に耐食性能が、それぞれの燃料電池で全く異なるためである。実際、使用されている材料も様々であり、黒鉛系素材から、Niクラッド材、高合金、ステンレス鋼と多様である。

【0006】商用化されているリン酸型燃料電池、熔融炭酸塩型燃料電池に使用されている材料を、固体高分子型燃料電池の構成材料に適用することは全く考えることができない。

【0007】図1は、固体高分子型燃料電池の構造を示す図で、図1(a)は、燃料電池セル(単セル)の分解図、図1(b)は燃料電池全体の斜視図である。同図に示すように、燃料電池1は単セルの集合体である。単セルは、図1(a)に示すように固体高分子電解質膜2の1面に燃料電極膜(アノード)3を、他面には酸化剤電極膜(カソード)4が積層されており、その両面にセパレータ5a、5bが重ねられた構造になっている。

【0008】代表的な固体高分子電解質膜2としては、水素イオン(プロトン)交換基を有するフッ素系イオン交換樹脂膜がある。

【0009】燃料電極膜3および酸化剤電極膜4には、粒子状の白金触媒と黒鉛粉、必要に応じて水素イオン交換基を有するフッ素樹脂からなる触媒層が設けられており、燃料ガスまたは酸化性ガスと接触するようになっている。

【0010】セパレータ5aに設けられている流路6aから燃料ガス(水素または水素含有ガス)Aが流されて燃料電極膜3に水素が供給される。また、セパレータ5bに設けられている流路6bからは空気のような酸化性ガスBが流され、酸素が供給される。これらガスの供給により電気化学反応が生じて直流電力が発生する。

【0011】アノード側: $H_2 \rightarrow 2H^+ + 2e^-$

カソード側: $(1/2)O_2 + 2H + 2e^- \rightarrow H_2O$

固体高分子型燃料電池セパレータに求められる機能は、

(1)燃料極側で、燃料ガスを面内均一に供給する“流路”としての機能、(2)カソード側で生成した水を、燃料電池より反応後の空気、酸素といったキャリアガスとともに効率的に系外に排出させる“流路”としての機能、(3)長時間にわたって電極として低電気抵抗、良電導性を維持する単セル間の電氣的“コネクタ”としての機能、および(4)隣り合うセルで一方のセルのアノード室と隣接するセルのカソード室との“隔壁”としての機能などである。

【0012】これまで、セパレータ材料としてカーボン板材の適用が鋭意検討されてきているが、カーボン板材には“割れやすい”という問題があり、さらに表面を平坦にするための機械加工コストおよびガス流路形成のための機械加工コストが非常に高くなる問題がある。それぞれが宿命的な問題であり、燃料電池の商用化そのものを難しくさせかねない状況がある。

【0013】カーボンの中でも、熱膨張性黒鉛加工品は格段に安価であることから、固体高分子型燃料電池セパレータ用素材として最も注目されている。しかしながら、ガス透過性を低減して前記隔壁としての機能を付与するためには、“複数回”に及ぶ樹脂含浸と焼成を実施しなければならない。また、平坦度確保および溝形成のための機械加工コスト等今後も解決すべき課題が多く、実用化されるに至っていないのが現状である。

【0014】こうした黒鉛系素材の適用の検討に対峙する動きとして、コスト削減を目的に、セパレータにステンレス鋼を適用する試みが開始されている。

【0015】特開平10-228914号公報には、金属製部材からなり、単位電池の電極との接触面に直接金めっきを施した燃料電池用セパレータが開示されている。金属製部材として、ステンレス鋼、アルミニウムおよびNi-鉄合金が挙げられており、ステンレス鋼としては、SUS304が用いられている。この発明では、

セパレータは金めっきが施されているので、セパレータと電極との接触抵抗が低下し、セパレータから電極への電子の導通が良好となるため、燃料電池の出力電圧が大きくなるとされている。

【0016】特開平8-180883号公報には、表面に形成される不動態膜が大気により容易に生成される金属材料からなるセパレータが用いられている固体高分子電解質型燃料電池が開示されている。金属材料としてステンレス鋼とチタン合金が挙げられている。この発明では、セパレータに用いられる金属の表面には、必ず不動態膜が存在しており、金属の表面が化学的に侵され難くなって燃料電池セルで生成された水がイオン化される度合いが低減され、燃料電池セルの電気化学反応度の低下が抑制されるとされている。また、セパレータの電極膜等に接触する部分の不動態膜を除去し、貴金属層を形成することにより、電気接触抵抗値が小さくなるとされている。

【0017】しかしながら、上記の公開公報に開示されている表面に不動態膜を備えたステンレス鋼のような金属材料をそのままセパレータに用いても、耐食性が十分でなく金属の溶出が起り、溶出金属イオンにより担持触媒性能が劣化（以下、担持触媒の被毒と記す）する。また、溶出後に生成するCr-OH、Fe-OHのような腐食生成物により、セパレータの接触抵抗が増加するという問題があるので、金属材料からなるセパレータには、コストを度外視した金めっき等の貴金属めっきが施されているのが現状である。

S: 0.005%以下、
V: 0.2%以下、
Cu: 0.2%以下、
Mo: 0~6%、

を含有し、かつ(Cr+3Mo)が10.5~43%の範囲内にある

(2) フェライト系ステンレス鋼中のSiおよびMnが、重量%で、Si量が0.3%以下、Mnが0.4%以下である上記(1)記載の固体高分子型燃料電池。

【0024】(3) フェライト系ステンレス鋼中のCおよびN量が、重量%で、C: 0.018%以下、N: 0.018%以下、かつCとNの合計含有量が、0.025%以下である上記(1)または(2)記載の固体高分子型燃料電池。

【0025】(4) フェライト系ステンレス鋼が、TiとNbの1種または2種を含有しており、Tiが、重量%で0.2%以下で、かつ6(C%+N%)~25(C%+N%)の範囲、およびNbが0.3%以下で、かつ6C%~25C%の範囲内にある上記(1)から(3)のいずれか記載の固体高分子型燃料電池。

【0026】なお、セパレータとは前述した4つの機能を有するものである。すなわち、a) 燃料極側で、燃料ガスを面内均一に供給する“流路”としての機能、b) カ

*【0018】これまでの金属材料のセパレータへの適用は、適用したという実績があるにすぎず、実用化にはほど遠い状況にある。

【0019】セパレータとして、高価な表面処理を施さない“無垢”で適用でき、電池環境での電気伝導性に優れると共に、耐食性に優れたステンレス鋼の開発がなされれば、燃料電池の製造コストが格段に低下し、固体高分子型燃料電池の商用化、用途拡大が期待できる。

【0020】

10 【発明が解決しようとする課題】本発明の課題は、高価な表面処理を施す必要がなく、溶出金属イオンによる各電極担持触媒の被毒が極めて少なく、かつ腐食生成物による電極との接触電気抵抗の増加および不動態皮膜の強化による接触抵抗の増加が少ないステンレス鋼のセパレータを備えた固体電解質型燃料電池を提供することにある。

【0021】

【課題を解決するための手段】本発明の要旨は、以下の通りである。

20 【0022】(1) 固体高分子電解質膜を中央にして燃料電極膜と酸化剤電極膜を重ね合わせた単位電池を複数個、単位電池間にセパレータを介在させて積層した積層体に、燃料ガスと酸化剤ガスを供給して直流電力を発生させる固体高分子型燃料電池において、セパレータが下記の化学組成を有するフェライト系ステンレス鋼からなることを特徴とする固体高分子型燃料電池。

* 【0023】重量%で、
P: 0.025%以下、
Ni: 0.2%以下、
Cr: 10.5~35%、
希土類元素: 0~0.1%

※ソード側で生成した水を、燃料電池より反応後の空気、酸素といったキャリアガスとともに効率的に系外に排出させる“流路”としての機能、c) 長時間にわたって電極として低電気抵抗、良電導性を維持する単セル間の電氣的“コネクタ”としての機能、およびd) 隣り合うセルで一方のセルのアノード室と隣接するセルのカソード室との“隔壁”としての機能を有するものである。これらの機能を複数枚のプレートで機能分担させる構造にする場合もある。本発明でいうセパレータとは、上記4つの機能のうちの少なくとも一つの機能を有するプレートをセパレータと言う。

【0027】本発明者らは、ステンレス鋼からなるセパレータを備えた固体高分子型燃料電池を開発するため、セパレータが置かれる環境において、ステンレス鋼表面から溶出する金属イオンを可能な限り低減することを目標に、単セルを用いて種々試験を実施した。その結果、以下の知見を得て本発明を完成するに至った

a) セパレータが置かれるpHが1~3の環境（以下、単にセパレータ環境と記す）において、オーステナイト

系ステンレス鋼は耐食性が不十分であり、金属の溶出が著しくセパレータには不適當である。

【0028】b) セパレータ環境で、フェライト系ステンレス鋼は良好な耐食性を発揮するが、一般のフェライト系ステンレス鋼では、電池性能に影響を及ぼす程度の金属の溶出が生じる。

【0029】c) 金属が溶出すると、腐食生成物(Feを主体とする水酸化物)が生成し、接触電気抵抗の増大をもたらす、かつ担持触媒性能に著しい悪影響を及ぼすので、起電力に代表される電池性能が短時間で劣化する。また、水素イオン(プロトン)交換基を有するフッ素系イオン交換樹脂膜の陽イオン伝導度にも悪影響を及ぼす。

【0030】d) 金属の溶出を防止するためには、フェライト系ステンレス鋼中の不純物のうち、S、P、V、NiおよびCuの含有量を同時に低減すると共に、不動態被膜を強固にしなければならない。

【0031】e) 不動態被膜を強固にしても、不動態被膜厚さを厚くすると接触電気抵抗が増大し、電池効率が著しく低下する。

【0032】f) 不動態被膜を厚くすることなく強固にして、セパレータ環境で金属の溶出を抑制するためには、CrとMoの含有量は(Cr%+3×Mo%)が12~43%の範囲内になるようにする必要がある。

【0033】g) 積極的にMoを添加することで、耐食性が確保されるが、Moは溶出したとしても、アノードおよびカソード部に担持されている触媒の性能に対する影響は比較的軽微である。

【0034】

【発明の実施の形態】以下、本発明の固体高分子型燃料電池が備えているフェライト系ステンレス鋼からなるセパレータの化学組成を規定した理由を詳しく説明する。なお、下記成分の%表示は重量%を示す。

【0035】S: 鋼中のS量は、0.005%以下とすることが必要である。Sは、鋼中共存元素および鋼中のS量に応じて、Mn系硫化物、Cr系硫化物、Fe系硫化物、Ti系硫化物、これらの複合硫化物および酸化物との複合非金属介在物としてほとんどは析出している。しかしながら、セパレータ環境においては、いずれの組成の非金属介在物も、程度の差はあるものの腐食の起点として作用し、不動態化の維持、金属の腐食溶出抑制に有害である。

【0036】また、燃料電池が作動している状況において、フェライト系ステンレス鋼からなるセパレータとMEA (Membrane Electrode Assembly) 間の隙間内は、電池反応および/または酸素濃度差電池腐食が起こることにより隙間内のpHが低下し、マイクロ電池腐食を起こしやすい状況となるが、硫化物系非金属介在物はその際の腐食起点、加速因子として大きな影響を及ぼす。通常の量産鋼の鋼中S量は、0.005%超え0.008%

前後であるが、上記の有害な影響を防止するためには0.005%以下に低減する必要がある。望ましい鋼中S量は0.002%以下であり、最も望ましい鋼中S量レベルは、0.001%未満であり、低ければ低い程よい。

【0037】P: 鋼中のP量は、0.025%以下であることが必要である。通常のスチンレス商用鋼含有レベルは、0.026~0.035%程度である。Pは不可避免的な不純物であり、Sと並んで、アノードおよびカソード触媒層の被毒に対して少なからずの影響を及ぼす有害素である。低い程望ましい。

【0038】V: 鋼中のVは、0.2%以下にする必要である。一般に、Vはステンレス鋼を溶製する際の必須溶解原料であるCr源中に不純物として含有されており、ある程度の混入は不可避である。但し、溶出したVは、アノードおよびカソード部に担持されている触媒の性能に対して少なからず悪影響を及ぼす。電池特性維持の上から、許容できる上限は0.2%であり、低ければ低いほどよい。

【0039】Cu, Ni: 鋼中のCu, Niは、いずれも、あるいは双方ともに0.2%以下にする必要がある。一般に不純物程度の微量Cu, Niであっても、低pH環境におけるステンレス鋼の耐食性を改善する効果を有する。しかしながら、セパレータ環境では、不動態維持状態における微量のCu, Niイオン溶出であってもアノードおよびカソード触媒層の被毒に対して影響を及ぼすので、上限を0.2%とする必要がある。スクラップからの混入も含めて、鋼中のCu, Ni量は低い方が望ましいが、0.2%以下の極微量不純物レベルのCu, Niが、フェライト系ステンレス鋼の不動態化能を高め、不動態化状態での金属溶出を抑制する作用も有し、結果として電池性能を改善するため、上限を0.2%とする。

【0040】Cr, Mo: Cr, Moはともに、耐食性を確保する上での基本合金元素である。含有量が高いほど高耐食となるが、高Cr化するに伴い常温韌性が低下する傾向があり、Cr量が35%を超えると量産での生産は困難となる。また、10.5%未満では、その他の元素を変化させてもセパレータとして必要な耐食性の確保が困難となる。

【0041】Moは、必要により含有させる元素で、Crに比べて少量で耐食性を改善する効果がある。0.5%未満ではMoの効果は明確でなくなる。含有させる場合、6%を超えて含有させると、シグマ相等の金属間化合物の析出回避が困難であり、鋼の脆化の問題から生産が困難となるので上限を5%とする。積極的にMo含有させることで、耐食性が確保される。Moは溶出したとしても、アノードおよびカソード部に担持されている触媒の性能に対する影響は比較的軽微であり、水素イオン(プロトン)交換基を有するフッ素系イオン交換樹脂膜

の陽イオン伝導度にも悪影響が小さい。

【0042】(Cr%+3Mo%)：セパレータ用ステンレス鋼としては、固体高分子型燃料電池の作動温度である70℃から高々100℃の環境において不動態化の状態にあり、かつ、継時的にも接触電気抵抗値が低いことが必要である。不動態皮膜厚さ増加と腐食生成物生成を実用的な範囲で抑制する必要がある。そのための必要条件として、CrおよびMoの含有量は、腐食指数である(Cr%+3Mo%)が12~43%の範囲内にあることが必要である。

【0043】実際の作動状態にある電池内部の模擬環境として妥当と判断される「25℃におけるpHが2.6の硫酸水溶液80℃中」で不動態化していることが少なくとも必要である。そのためには、本環境で0.2V vs. SCEにおける不動態維持電流密度が50μA/cm²未満であることが望ましい。

【0044】Si：鋼中のSi量は、0.3%以下にするのが好ましい。Siは量産鋼においてはAlと同様に有効な脱酸元素である。しかし、溶出したSiが、アノードおよびカソード触媒層の被毒に対して少なからず影響を及ぼすため、電池特性維持の上からは明らかに有害であるため0.3%以下とする。0.25%前後での生産が量産コスト低減の観点からは最も望ましいが、セパレータ環境では0.2%未満であることが望ましい。さらに望ましいのは、0.1%未満である。

【0045】Mn：鋼中Mn量は、0.4%以下とするのが望ましい。通常、Mnは、鋼中のSをMn系の硫化物として固定する作用があり、熱間加工性を改善する効果がある。また脱酸元素あるいはNiバランス調整元素として積極的に添加してもよい。しかし、不動態を維持している状態においても金属の溶出がわずかつ進行するが、0.4%を超える量になると、溶出したMnイオンが、アノードおよびカソード触媒層の被毒に対して少なからず影響を及ぼす。望ましくは、0.1%未満である。0.45以下のMnであれば、量産の際の熱間割れなどの問題も発生することなく製造が可能である。製造コストアップもほとんど問題とならない。

【0046】C、N：鋼中のC、Nは、常温韌性改善の目的から、Cは0.018%以下、Nは0.018%以下で、かつC%+N%値で0.025%以下とすることが望ましい。C、Nは、浸入型元素であり、高純度フェライト系ステンレス鋼の母材韌性、溶接部の耐食性および韌性劣化の原因となる。C、Nは厳しく制限することが、高純度フェライト系ステンレス鋼の熱延コイルの製造工程で問題となる常温韌性対策となり、製造コストの

上昇を避けることができる。鋼中のC、Nを極低化すればするほど常温韌性は改善するので低ければ低いほどよい。

【0047】Ti：Tiは、必要により0.2%以下で、(C%+N%)値の6倍以上、25倍以下の範囲量で含有させる。Tiは、アノードおよびカソード触媒層に被毒を及ぼすので、本来は低減されるべき元素であるが、量産での製造性確保、薄板の加工性確保の観点より、必要により最低量含有させる。

10 【0048】溶接性が要求されない場合には、(C%+N%)値×6倍以上、10倍以下が最も望ましい。溶接性が求められる場合には、(C%+N%)値の10倍以上、16倍以下が最も望ましい。介在物起因の板表面疵発生を回避するためには、0.1%以下とすることが望ましい。必要以上含有させると、不動態維持状態における金属の溶出によるアノードおよびカソード触媒性能劣化の原因となる。

【0049】Nb：Nbは、必要により含有させる元素で、Tiと同様に鋼中C、Nとの結合力がCrよりも強い合金元素である。Nbは、0.3%以下で、かつC%×6~C%×25〔すなわち、Nb(%) / C(%) = 6~25%〕の範囲内で含有させる。熱延コイルの常温韌性を含め韌性改善に極めて効果的である。ただし、腐食に伴い溶出したNbは、腐食面に腐食生成物として堆積し、接触電気抵抗を高める弊害があるので、母材性能の観点のみからはNb含有量は低い方が望ましい。ただし、溶接部の性能の確保や、NbとTiを同時に含有させて冷延鋼板素材の加工性を改善する必要があると判断される場合には必要最少量添加する。

30 【0050】希土類元素(REM)：希土類元素は、溶鋼段階でSとの結合力が極めて強いので、Sを無害化する効果がある。したがって、必要によりミッシュメタルのような形で添加しても良い。含有量は、0.1%以下で十分効果が得られる。

【0051】上記元素以外の元素を必要により含有させてもよい。例えば、熱間加工性改善には、0.1以下のCa、MgやBを含有させるのがよい。

【0052】

【実施例】表1に示した28種の化学組成のフェライト系ステンレス鋼を高周波誘導加熱方式の150kg真空溶解炉で溶解した。溶解原料としては、市販の不純物の少ない原料を厳選して使用し、鋼中の不純物量を調整した。

【0053】

【表1】

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12

| 表1 | | | | | | | | | | | | | | | | (重量%, 残部Fe) | | | |
|-----|--------|------|------|--------|---------|--------|--------|------|--------|------|--------|-------|-------|---------|--------|-------------|---------|--------|------|
| No. | C | Si | Mn | P | S | Cu | Ni | Cr | Mo | Ti | V | N | Al | その他 | C+N | 6(C+N) | 25(C+N) | Cr+3Nb | |
| 1 | 0.0025 | 0.08 | 0.08 | 0.012 | 0.0008 | 0.008 | 0.003 | 17.8 | 0.82 | 0.10 | 0.007 | 0.005 | 0.012 | | 0.0075 | 0.0450 | 0.1875 | 20.06 | 本発明例 |
| 2 | 0.0018 | 0.12 | 0.08 | 0.010 | 0.0008 | 0.008 | 0.004 | 18.3 | 0.82 | 0.10 | 0.008 | 0.005 | 0.010 | | 0.0068 | 0.0408 | 0.1700 | 20.76 | |
| 3 | 0.0019 | 0.16 | 0.06 | 0.011 | 0.0006 | 0.006 | 0.003 | 19.5 | 1.20 | 0.11 | 0.006 | 0.005 | 0.008 | | 0.0069 | 0.0414 | 0.1725 | 23.10 | |
| 4 | 0.0022 | 0.15 | 0.09 | 0.012 | 0.0009 | 0.005 | 0.005 | 20.5 | 1.81 | 0.10 | 0.008 | 0.006 | 0.011 | | 0.0082 | 0.0492 | 0.2050 | 25.93 | |
| 5 | 0.0013 | 0.10 | 0.10 | 0.011 | 0.0008 | 0.008 | 0.004 | 25.6 | 0.98 | 0.12 | 0.007 | 0.005 | 0.010 | | 0.0063 | 0.0378 | 0.1575 | 28.54 | |
| 6 | 0.0020 | 0.08 | 0.08 | 0.012 | 0.0009 | 0.005 | 0.005 | 18.5 | 0.52 | 0.11 | 0.006 | 0.004 | 0.011 | | 0.0060 | 0.0360 | 0.1500 | 20.08 | |
| 7 | 0.0018 | 0.08 | 0.08 | 0.010 | 0.0006 | 0.005 | 0.005 | 19.2 | 1.82 | 0.11 | 0.008 | 0.006 | 0.012 | | 0.0078 | 0.0468 | 0.1950 | 24.65 | |
| 8 | 0.0016 | 0.10 | 0.08 | 0.011 | 0.0007 | 0.005 | 0.004 | 19.5 | 2.82 | 0.11 | 0.007 | 0.005 | 0.010 | | 0.0088 | 0.0396 | 0.1650 | 27.98 | |
| 9 | 0.0012 | 0.09 | 0.10 | 0.012 | 0.0008 | 0.006 | 0.003 | 29.2 | 4.02 | 0.11 | 0.005 | 0.005 | 0.013 | | 0.0062 | 0.0372 | 0.1550 | 41.28 | |
| 10 | 0.0028 | 0.11 | 0.09 | 0.010 | 0.0008 | 0.013 | 0.003 | 19.2 | 1.88 | 0.10 | 0.008 | 0.005 | 0.012 | La:0.08 | 0.0076 | 0.0456 | 0.1900 | 24.84 | |
| 11 | 0.0025 | 0.10 | 0.10 | 0.009 | 0.0009 | 0.012 | 0.012 | 19.2 | 2.02 | - | 0.008 | 0.006 | 0.010 | | 0.0085 | 0.0510 | 0.2125 | 25.26 | |
| 12 | 0.0016 | 0.08 | 0.06 | 0.007 | 0.0007 | 0.012 | 0.015 | 19.0 | 0.82 | - | 0.005 | 0.005 | 0.011 | | 0.0068 | 0.0396 | 0.1650 | 21.46 | |
| 13 | 0.0015 | 0.08 | 0.08 | 0.006 | 0.0003 | 0.011 | 0.015 | 19.3 | 1.95 | - | 0.008 | 0.005 | 0.012 | | 0.0065 | 0.0390 | 0.1625 | 25.15 | |
| 14 | 0.0016 | 0.08 | 0.08 | 0.008 | 0.0008 | 0.013 | 0.016 | 18.9 | 2.86 | - | 0.008 | 0.005 | 0.013 | | 0.0065 | 0.0390 | 0.1625 | 27.48 | |
| 15 | 0.0022 | 0.32 | 0.43 | 0.008 | 0.0005 | 0.010 | 0.012 | 22.3 | 1.82 | - | 0.003 | 0.003 | 0.010 | | 0.0062 | 0.0312 | 0.1300 | 27.76 | |
| 16 | 0.0025 | 0.08 | 0.08 | 0.007 | 0.0070* | 0.010 | 0.011 | 16.8 | - * | - | 0.120 | 0.008 | 0.010 | | 0.0105 | 0.0630 | 0.2625 | 16.80 | 比較例 |
| 17 | 0.0022 | 0.28 | 0.09 | 0.007 | 0.0075* | 0.010 | 0.008 | 16.5 | - * | - | 0.120 | 0.007 | 0.009 | | 0.0092 | 0.0552 | 0.2300 | 16.50 | |
| 18 | 0.0020 | 0.08 | 0.45 | 0.008 | 0.0065* | 0.009 | 0.009 | 16.8 | - * | - | 0.110 | 0.007 | 0.010 | | 0.0090 | 0.0540 | 0.2250 | 16.80 | |
| 19 | 0.0016 | 0.08 | 0.07 | 0.029* | 0.0088* | 0.010 | 0.010 | 16.8 | - * | - | 0.130 | 0.006 | 0.008 | | 0.0076 | 0.0456 | 0.1900 | 15.80 | |
| 20 | 0.0015 | 0.30 | 0.45 | 0.028* | 0.0065* | 0.150 | 0.120 | 16.7 | - * | - | 0.110 | 0.007 | 0.010 | | 0.0085 | 0.0510 | 0.2125 | 16.70 | |
| 21 | 0.0038 | 0.05 | 0.08 | 0.007 | 0.0058* | 0.750* | - | 19.2 | - * | - | 0.110 | 0.005 | 0.008 | | 0.0088 | 0.0528 | 0.2200 | 19.20 | |
| 22 | 0.0041 | 0.08 | 0.08 | 0.008 | 0.0065* | - | 0.152 | 19.0 | - * | - | 0.110 | 0.008 | 0.009 | | 0.0101 | 0.0608 | 0.2525 | 19.0 | |
| 23 | 0.0200 | 0.05 | 0.08 | 0.006 | 0.0072* | - | - | 19.2 | 1.80 | - | 0.120 | 0.009 | 0.018 | | 0.0290 | 0.1740 | 0.7250 | 24.6 | |
| 24 | 0.0250 | 0.45 | 0.50 | 0.028* | 0.0085* | 0.120 | 0.080 | 11.5 | 0.02 * | - | 0.110 | 0.020 | 0.002 | Nb:0.48 | 0.0450 | 0.2700 | 1.1250 | 11.56 | |
| 25 | 0.0280 | 0.25 | 0.45 | 0.030* | 0.0075* | 0.120 | 0.100 | 16.8 | 0.02 * | - | 0.250* | 0.023 | 0.003 | | 0.0510 | 0.3080 | 1.2750 | 16.86 | |
| 26 | 0.0580 | 0.34 | 1.20 | 0.030* | 0.0061* | 0.230* | 8.210* | 18.5 | 0.08 * | - | 0.080 | 0.031 | 0.002 | | 0.0890 | 0.5340 | 2.2250 | 18.74 | |
| 27 | 0.0130 | 0.62 | 1.00 | 0.028* | 0.0062* | 0.240* | 12.30* | 17.5 | 2.24 | - | 0.070 | 0.023 | 0.003 | | 0.036 | 0.2160 | 0.9000 | 24.22 | |
| 28 | " | " | " | " | " | " | " | " | " | - | " | " | " | | " | " | " | 24.22 | |
| 29 | 0.0230 | 0.24 | 0.53 | 0.025 | 0.0230 | 0.080 | 0.020 | 10.1 | - | - | 0.030 | 0.005 | 0.002 | | 0.028 | 0.168 | 0.7000 | 10.10 | |

* 本発明で規定する範囲外を示す

【0054】造塊した横断面が丸形のインゴットは、大気中で1230℃に3時間加熱した後、プレス方式鍛造機で熱間鍛造し、各インゴットを下記2種の寸法の試験用スラブに仕上げた。

【0055】①厚さ30mm、幅100mm、長さ120mm

②厚さ70mm、幅380mm、長さ550mm

①のスラブは、熱間圧延して厚さ6mmの熱延鋼板とし、次いで量産での熱延終了直後の温度履歴を模擬した断熱材巻き付け条件で徐冷した。常温での熱延コイル巻*30

① 表1のNo.25の熱延鋼板

② 表1のNo.11~15、16~23の熱延鋼板..... 900℃

③ 表1のNo.1~10の熱延鋼板..... 930℃

④ 表1のNo.24、29の熱延鋼板..... 980℃

⑤ 表1のNo.26、27の熱延鋼板..... 1080℃

各温度は、再結晶が進行し、金属間化合物が固溶する温度とした。在炉時間はおよそ20分であった。

【0057】次いで、溶体化処理した熱延鋼板を、多段式ゼンジマー型ロール圧延機を用い途中で中間焼鈍を挟みながら、冷間圧延をおこない厚さ0.3mmに仕上げた。最終仕上げ焼鈍は、露点が-50℃以下である水素雰囲気光輝焼鈍炉内で行い、温度は熱間圧延素材の焼鈍温度と同じとした。保持時間は1分であり、在炉時間で約3分であった。

【0058】この冷間圧延焼鈍材から、下記寸法のセパレータ模擬環境での不動態皮膜の評価をおこなうための試験片、および実際の固体高分子型燃料電池への装填用のセパレータをプレス成形により製作した。

【0059】なお、比較例のNo.27については、模擬環境用試験片およびセパレータを作製後、片面5μm厚 ※50

*性を調べるためシャルピー衝撃試験に供した。試験片は、JIS Z2202 4号ハーフサイズとした。②のスラブは、機械加工でスラブ表面を切削加工して、表面の酸化スケールを除去し、厚さ62mmのスラブに仕上げた。このスラブを大気中で1200℃に加熱し、熱間圧延して厚さ4mmに仕上げた後、①と同様、量産での熱延終了直後の温度履歴を模擬した断熱材巻き付け条件で徐冷した。

【0056】この熱延鋼板に、化学組成に応じて下記の温度で、保持4分の溶体化処理を施し、強制空冷した。

..... 830℃

※さの金めっきを施した。

【0060】模擬環境用試験片：厚さ0.3mm、幅10mm、長さ10mm

セパレータ：厚さ0.3mm、縦80mm、横80mm
ガス流路：高さ0.8mm、山と山との間隔1.2mm
(コルゲート加工)これらの表面をショット加工用SiC砥粒を用いて機械的にショット研磨仕上げし、5%HNO₃+3%HF、40℃中で15分間の超音波洗浄を行い、さらに、試験直前に6%水酸化ナトリウム水溶液を用いたアルカリ噴霧脱脂処理をおこない、流水で簡易水洗後、バッチ型水槽で蒸留水浸漬洗浄を3回行い、さらに蒸留水噴霧洗浄を4分間行って冷風ドライヤー乾燥させた後、各試験に供した。

【0061】模擬環境での試験として、特級試薬の硫酸を用いて調整した25℃におけるpHが2.6である硫

酸水溶液を80℃に昇温し、その溶液中に試験片を6時間浸漬し、不働態化の有無を腐食減量、素材表面からの水素気泡発生、試験溶液の色変化から評価すると共に、金属の溶出程度をより正確に調べるため、0.2V vs SCE における不働態保持電流密度を測定した。

*【0062】シャルピー衝撃試験結果およびセパレータ模擬環境における試験結果は、表2に示す通りであった。

【0063】

* 【表2】

| No | 25℃におけるpHが2.6である硫酸水溶液80℃での評価 | | 固体電解質型燃料電池セル装填による評価 | | 正延後空冷した熱延鋼板の常温(25℃)での衝撃値 (試験片: JIS-4号ハブパイプ (kgf-m/cm ²)) | 備考 |
|----|------------------------------|------------------------------------------------|-------------------------------------|--|----------------------------------------------------------------------------|------|
| | 不働態化の有無 | 0.2V vs. SCEにおける不働態保持電流密度(μA/cm ²) | 1時間経過後の単セル電圧低下率 1-(経過後電圧V/初期電圧v) | | | |
| 1 | 有り | 10 ~ 20 | <0.05 | | >15 | 本発明例 |
| 2 | " | 20 ~ 30 | <0.05 | | >15 | |
| 3 | " | 10 ~ 20 | <0.05 | | >15 | |
| 4 | " | 10 ~ 20 | <0.05 | | >15 | |
| 5 | " | 10 ~ 20 | <0.05 | | >15 | |
| 6 | " | 10 ~ 20 | <0.05 | | >15 | |
| 7 | " | <10 | <0.05 | | >15 | |
| 8 | " | <10 | <0.05 | | >15 | |
| 9 | " | <10 | <0.05 | | >15 | |
| 10 | " | 10 ~ 20 | <0.05 | | >15 | |
| 11 | " | 10 ~ 20 | <0.05 | | >15 | |
| 12 | " | <10 | <0.05 | | >15 | |
| 13 | " | <10 | <0.05 | | >15 | |
| 14 | " | <10 | <0.05 | | >15 | |
| 15 | " | <10 | <0.05 | | >15 | |
| 16 | 無し | 50 ~ 70 | 0.3 ~ 0.5 | | 2 | 比較例 |
| 17 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 2 | |
| 18 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 3 | |
| 19 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 2 | |
| 20 | " | 50 ~ 70 | 0.3 ~ 0.8 | | 2 | |
| 21 | 有り | 50 ~ 70 | 0.3 ~ 0.5 | | 3 | |
| 22 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 3 | |
| 23 | " | 50 ~ 70 | 0.5 ~ 0.7 | | 1 | |
| 24 | " | >1mA/cm ² | >0.8 | | 12 | |
| 25 | " | 50 ~ 70 | >0.8 | | 12 | |
| 26 | " | 10 ~ 20 | >0.8 | | 25 | |
| 27 | " | 10 ~ 20 | >0.8 | | 28 | |
| 28 | " | <10 | <0.05 | | 28 | |
| 29 | " | >1mA/cm ² | >0.8 | | 18 | |

【0064】表2から明らかなように、本発明例では、80℃に昇温した25℃におけるpHが2.6である硫酸水溶液中で不働態化状態にあり、溶出の程度を示す“不働態保持電流密度”も20μA/cm²以下となっている。

【0065】ステンレス鋼を固体高分子型燃料電池用セパレータとして適用する際には、不働態保持電流密度は可能な限り低いレベルとすることが望ましいことはいまでもない。安定して低い値をとることが重要であり、10μA/cm²未満が最も望ましく、次いで10~20μA/cm²であることが望ましい。

【0066】比較例の不働態電流密度は、30~80μA/cm²であり、抑制されているといえるが、セパレータから比較的大きな溶出が起こっている状態であることを示している。

【0067】本発明者らは、燃料電池用セパレータ材料としての適用可否を判断する基準として、実機単セル電池での性能特性との関係から不働態保持電流密度>50μA/cm²では性能が不十分であると判断した。不働態保持電流密度が50μA/cm²以下の材料においては、実単セル評価試験でも、問題となる程度の継続的性能劣化を確認するには至っておらず、迅速模擬環境評価条件として極めて適切であると判断している。本結果においても、発明例の場合は固体高分子型燃料電池環境※50

※で最も望ましい金属素材のひとつである金めっき素材(供試鋼27)と同じレベルであり、相対的に見て良好な性能が確保できると判断された。

【0068】次に、実際の固体高分子型単セル電池内部にセパレータとして装填した状態での特性評価として、電池内に燃料ガスを流してから1時間経過後に単セル電池の電圧を測定し、初期の電圧と比較することにより電圧の低下率を調べた。なお、低下率は、1-(1時間経過後の電圧V/初期電圧v)により求めた。

【0069】評価に用いた固体高分子型燃料電池は、米国Electrochem社製市販電池セルFC50を改造して用いた。

【0070】アノード極側燃料用ガスとしては99.9999%水素ガスを用い、カソード極側ガスとしては空気をを用いた。電池本体は全体を78±2℃に保温すると共に、電池内部の湿度制御を、セル出側の排ガス水分濃度測定をもとに入り側で調整した。電池内部の圧力は、1気圧である。水素ガス、空気の電池への導入ガス圧は0.04~0.20barで調整した。セル性能評価は、単セル電圧で500mA/cm²-0.62Vが確認できた状態より継続的に測定を行った。

【0071】単セル性能測定用システムとしては、米国スクリプナー社製890 シリーズを基本とした燃料電池計測システムを改造して用いた。電池運転状態により、特

性に変化があると予想されるが、同一条件での比較評価である。

【0072】結果を表2に示した。

【0073】表2から明らかなように、本発明例では電圧低下率は全て0.05以下であり、No.27の高価で高耐食性の金めっきしたセパレータと同等となった。また、本発明で規定した化学組成を外れた比較例では、電圧低下率が0.3~0.8と極めて大きかった。

【0074】一部の試験片で、長時間の試験を実施して評価おこなったが、表2に示した短時間試験結果と近似した相関した結果が得られた。

【0075】ステンレス鋼の常温での靱性は、一般にオーステナイト系ステンレス鋼に比べてフェライト系ステンレス鋼は劣っている。しかし、表2のシャルピー試験結果から明らかなように、鋼中のC、N含有量が高い比較例の場合に比べて、C、N含有量が低い一連の本発明例の場合は格段に優れた靱性を有している。一般に常温靱性は、板厚が薄くなると見かけ上改善されるため、本発明の場合のレベルであれば実用上全く問題がない。すなわち、高純度フェライト系ステンレス鋼製造時に問題となる熱延コイルの常温靱性は良好であると言える。一般に常温靱性は、板厚が薄くなると見かけ上改善されるため、本発明の鋼のレベルであれば実用上全く問題がな

い。

【0076】

【発明の効果】本発明の固体高分子型燃料電池は、セパレータがフェライト系ステンレス鋼からなり、高価な金めっきを施す必要ないので、安価に製造ができる。

【図面の簡単な説明】

【図1】固体高分子型燃料電池の構造を示す図である。

【符号の説明】

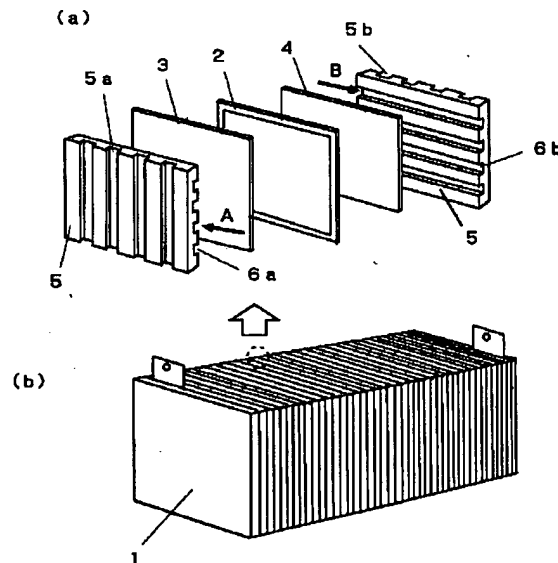
- 1 燃料電池
- 2 固体分子電解質膜
- 3 燃料電極膜
- 4 酸化剤電極膜
- 5 a、5 b セパレータ

【要約】

【課題】溶出金属イオンによる各電極担持触媒の被毒が極めて少ないステンレス鋼のセパレータを備えた固体電解質型燃料電池を提供する。

【解決手段】S、P、V、NiおよびCu等の不純物を低くし、CrとMoの含有量を、Cr:10.5~35%、Mo:0.5~5%で、かつ $12\% \leq Cr + 3Mo \leq 43\%$ を満足させたステンレス鋼からなるセパレータを備えた固体電解質型燃料電池。

【図1】



フロントページの続き

(56)参考文献 特開 平6-146006 (JP, A)
特開 平8-188853 (JP, A)
特開 平8-311620 (JP, A)
特開 平9-157801 (JP, A)
特開 平9-241809 (JP, A)
特開 平10-280103 (JP, A)

(58)調査した分野(Int.Cl.⁷, DB名)

H01M 8/02
H01M 8/10
C22C 38/00 302
C22C 38/46
C22C 38/50

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CLAIMS

[Claim(s)]

[Claim 1] The solid-state macromolecule type fuel cell to which separator is characterized by the bird clapper from the ferritic stainless steel which has the following chemical composition in the solid-state macromolecule type fuel cell which fuel gas and oxidizer gas are supplied [fuel cell] to the layered product which separator was made to intervene between unit cells and carried out the laminating of two or more unit cells on top of which the solid-state polyelectrolyte film was carried out in the center, and the fuel electrode layer and the oxidizer electrode layer were laid, and generates a direct current power.

With weight % S:0.005% or less P:0.025% or less V:0.2% or less Less than [nickel:0.2%] Less than [Cu:0.2%]

Cr:10.5-35% Mo:0-6% Rare earth elements: Contain 0 - 0.1%, and (Cr+3Mo) be in 10.5 - 43% of within the limits. [Claim 2]

The solid-state macromolecule type fuel cell according to claim 1 to which the amount of Si is characterized by Si and Mn in a ferritic stainless steel being [0.3% or less and Mn] 0.4% or less in weight %.

[Claim 3] The solid-state macromolecule type fuel cell according to claim 1 or 2 whose sum total content of C:0.018% or less, N:0.018% or less, and C and N C in a ferritic stainless steel and the amount of N is 0.025% or less in weight %.

[Claim 4] The claims 1-3 which the ferritic stainless steel contains one sort of Ti and Nb or two sorts, and Ti is 0.2% or less in weight %, and the range of 6 (C-% +N %)-25 (C-% +N %) and whose Nb are 0.3% or less, and are in 6C% - 25C% of within the limits are the solid-state macromolecule type fuel cells of a publication either.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the solid-state macromolecule type fuel cell used as small distributed power supplies, such as an object for automobile loading, and home use.

[0002]

[Description of the Prior Art] A fuel cell is a cell which generates a direct current power using hydrogen and oxygen, and has a solid oxide fuel cell, a fused carbonate fuel cell, a phosphoric acid fuel cell, a solid-state macromolecule type fuel cell, etc. The name of a fuel cell originates in the component of the "electrolyte" portion which makes the basis of a cell.

[0003] Now, there are a phosphoric acid fuel cell and a fused carbonate fuel cell in the fuel cell which has reached the commercial stage. The operating temperature with a near fuel cell is [in a solid oxide fuel cell / in 1000 degrees C and a fused carbonate fuel cell] 80 degrees C at 650 degrees C and a phosphoric acid fuel cell in 200 degrees C and a solid-state macromolecule type fuel cell.

[0004] An operating temperature is as low as 80-degree-C order, deactivation is easy and, as for the solid oxide fuel cell, utilization is globally expected considering distributed power supplies for emergencies, such as a small place of business since energy efficiency can also expect about 40%, and the central office, the home small distribution power supply which uses town gas as fuel, hydrogen gas, the methanol, or the gasoline as a power supply for low-pollution electric vehicle loading used as fuel.

[0005] Although various kinds of above-mentioned fuel cells are called by the common name called "fuel cell", when considering each cell component, they need to completely regard as a different thing. The performance called for by sublimation of the existence of the corrosion of the component by the electrolyte used, the existence of the high temperature oxidation which it begins to actualize from near 380 degree C, and an electrolyte, the existence of a re-deposit and condensation, etc., especially an anti-corrosion performance are because it completely differs by each fuel cell. The material currently used is also actually various and it is as various as nickel clad plate from a graphite system material, a high alloy, and stainless steel.

[0006] It is unthinkable to apply the material currently used for the phosphoric acid fuel cell commercialized and the fused carbonate fuel cell to the component of the quality type fuel cell of a solid-state macromolecule at all.

[0007] Drawing 1 is drawing showing the structure of a solid-state macromolecule type fuel cell, drawing 1 (a) is the exploded view of a fuel cell (single cell), and drawing 1 (b) is the perspective diagram of the whole fuel cell. As shown in this drawing, a fuel cell 1 is the aggregate of a single cell. a single cell is shown in drawing 1 (a) -- as -- the 1st page of the solid-state polyelectrolyte film 2 -- the fuel electrode layer (anode) 3 -- on the other hand -- being alike -- the laminating of the oxidizer electrode layer (cathode) 4 is carried out, and it has structure which Separator 5a and 5b put on the both sides

[0008] As a typical solid-state polyelectrolyte film 2, there is a fluorine system ion-exchange-resin film which has a hydrogen ion (proton) exchange group.

[0009] The catalyst bed which consists of a fluororesin which has a hydrogen ion exchange group a particle-like platinum catalyst, graphite powder, and if needed is prepared in the fuel electrode layer 3 and the oxidizer electrode layer 4, and fuel gas or a oxidizing gas is contacted.

[0010] Passage 6a to fuel gas (hydrogen or hydrogen content gas) A prepared in separator 5a is passed, and hydrogen is supplied to the fuel electrode layer 3. Moreover, from passage 6b prepared in separator 5b, oxidizing gas B like air is passed and oxygen is supplied. Electrochemical reaction arises by supply of these gas, and a direct current power occurs.

[0011] anode side : $H_2 \rightarrow 2H^+ + 2e^-$ cathode side : $(1/2) O_2 + 2H^+ \rightarrow H_2O$ solid-state macromolecule type fuel cell separator is asked (1) The function as "passage" which supplies fuel gas to the homogeneity within a field by the fuel-electrode side, (2) The function as "passage" to make the water generated by the cathode side discharge out of a system efficiently with carrier gas, such as air after a reaction, and oxygen, from a fuel cell, (3) (4) 4 [the function as electric" connector / between the single cells which maintain low electric resistance and right conductivity as an electrode over a long time /, and] It is a function as a "septum" with the cathode room of the cell which adjoins the anode room of one cell in an adjacent cell etc.

[0012] Although application of a carbon plate has been wholeheartedly considered as a separator material until now, there is a problem of "being easy to be divided" into a carbon plate, and there is a problem to which the machining cost for the machining cost for making a front face flat further and gas-passageway formation becomes very high. Each is a fatal problem

and there is a situation that the commercialization of a fuel cell itself may be made difficult.

[0013] also in carbon, a thermal-expansion nature graphite workpiece is boiled markedly, and since it is cheap, it attracts attention most as a material for solid-state macromolecule type fuel cell separator. However, in order to reduce gas permeability and to give the function as the aforementioned septum, you have to carry out resin sinking in and baking which attain to "multiple times." Moreover, the present condition is that there are many technical problems which should also be solved from now on [, such as machining cost for flatness reservation and slot formation,], and they have come to be put in practical use.

[0014] As movement which stands face to face against examination of application of such a graphite system material, the attempt which applies stainless steel to separator is started for the purpose of cost reduction.

[0015] It becomes JP,10-228914,A from a metal member, and the separator for fuel cells which gave direct gilding to the contact surface with the electrode of a unit cell is indicated. As a metal member, stainless steel, aluminum, and nickel-iron alloy is mentioned, and SUS304 is used as stainless steel. In this invention, since gilding is given, the contact resistance of separator and an electrode falls and the flow of the electron to an electrode becomes good from separator, it is supposed that the output voltage of a fuel cell becomes separator large.

[0016] The solid-state polyelectrolyte type fuel cell for which the separator with which the passive-state film formed in a front face becomes JP,8-180883,A from the metallic material easily generated by the atmosphere is used is indicated. Stainless steel and the titanium alloy are mentioned as a metallic material. In the front face of the metal used for separator in this invention, the degree by which the water which the passive-state film surely existed, became [the metaled front face] is hard to be invaded chemically, and was generated in the fuel cell cell is ionized is reduced, and it is supposed that the fall which is the degree of electrochemical reaction of a fuel cell cell will be suppressed. Moreover, it is supposed by removing non-***** of a portion in contact with the electrode layer of separator etc., and forming a noble-metals layer that electric contact resistance will become small.

[0017] However, even if it uses for separator a metallic material like the stainless steel which equipped with the passive-state film the front face currently indicated by the above-mentioned open official report as it is, corrosion resistance is not enough, metaled elution takes place, and a support catalyst performance deteriorates by the elution metal ion (it is hereafter described as poisoning of a support catalyst). Moreover, the present condition is that noble-metals plating, such as gilding which ignored cost to the separator which consists of a metallic material by corrosion product like Cr-OH and Fe-OH which are generated after elution since there was a problem that the contact resistance of separator increased, is performed.

[0018] The actual result of having applied does not pass over the application to the separator of an old metallic material for it to be, but is in a situation far from utilization.

[0019] if the development of the stainless steel which was excellent in corrosion resistance while it was "pure", being able to apply and excelling in the electrical conductivity in cell environment which does not perform expensive surface treatment as separator is made, the manufacturing cost of a fuel cell is markedly alike, and falls, and commercialization of a solid-state macromolecule type fuel cell and use expansion can be expected

[0020]

[Problem(s) to be Solved by the Invention] The technical problem of this invention is to offer the solid oxide fuel cell equipped with the separator of stainless steel with few [it is not necessary to perform expensive surface treatment, and there is very little poisoning of each electrode support catalyst by the elution metal ion, and] increases in the contact resistance by the increase in the contact electricity resistance with the electrode by the corrosion product, and strengthening of a passive-state coat.

[0021]

[Means for Solving the Problem] The summary of this invention is as follows.

[0022] (1) The solid-state macromolecule type fuel cell to which separator is characterized by the bird clapper from the ferritic stainless steel which has the following chemical composition in the solid-state macromolecule type fuel cell which fuel gas and oxidizer gas are supplied [fuel cell] to the layered product which separator was made to intervene between unit cells and carried out the laminating of two or more unit cells on top of which the solid-state polyelectrolyte film was carried out in the center, and the fuel electrode layer and the oxidizer electrode layer were laid, and generates a direct current power.

[0023]

By weight % S:0.005% or less, P:0.025% or less, V:0.2% or less, nickel: Less than [0.2%], Cu: Less than [0.2%], Cr: 10.5-35%, Mo: 0-6%, Rare earth elements: The solid-state macromolecule type fuel cell of the above-mentioned (1) publication 0.3% or less and whose Mn the amount of Si is 0.4% or less in weight % for Si and Mn in (2) ferritic stainless steels which contain 0 - 0.1%, and (Cr+3Mo) are in 10.5 - 43% of within the limits.

[0024] (3) A solid-state macromolecule type fuel cell the above (1) whose sum total content of C:0.018% or less, N:0.018% or less, and C and N C in a ferritic stainless steel and the amount of N is 0.025% or less in weight %, or given in (2).

[0025] (4) (3) is the solid-state macromolecule type fuel cell of a publication either from the above (1) which the ferritic stainless steel contains one sort of Ti and Nb, or two sorts, and Ti is 0.2% or less in weight %, and the range of 6 (C-% +N %)-25 (C-% +N %) and whose Nb are 0.3% or less, and is in 6C% - 25C% of within the limits.

[0026] In addition, separator has four functions mentioned above. Namely, the function as "passage" which supplies fuel gas to the homogeneity within a field by a fuel-electrode side, b) The function as "passage" to make the water generated by the cathode side discharge out of a system efficiently with carrier gas, such as air after a reaction, and oxygen, from a fuel cell, c) It has a function as electric "connector" between the single cells which maintain low electric resistance and right conductivity

as an electrode over a long time, and a function as a "septum" with the cathode room of the cell which adjoins the anode room of one cell in a cell d Adjacent. These functions may be made into the structure which carries out a functional assignment on two or more plates. The separator as used in the field of this invention says as separator the plate which has at least one of the four above-mentioned functions.

[0027] In order that this invention persons might develop the solid-state macromolecule type fuel cell equipped with the separator which consists of stainless steel, in the environment where separator is placed, for the purpose of reducing the metal ion eluted from a stainless steel front face as much as possible, they used the single cell and examined many things.

Consequently, in the environment (it is only hereafter described as separator environment) of 1-3, pH on which a separator is placed [which acquires the following knowledge and came to complete this invention] has inadequate corrosion resistance, and an austenitic stainless steel's is [metaled elution] remarkably unsuitable to separator.

[0028] b) Although a ferritic stainless steel demonstrates good corrosion resistance in a separator environment, in a general ferritic stainless steel, elution of the metal of the grade which affects a cell performance arises.

[0029] c) If a metal is eluted, since a corrosion product (hydroxide which makes Fe a subject) generates, and it will bring about increase of the contact electricity resistance and will have a remarkable bad influence on a support catalyst performance, the cell performance represented by electromotive force deteriorates for a short time. Moreover, it has a bad influence also on the cation conductivity of a fluorine system ion-exchange-resin film which has a hydrogen ion (proton) exchange group.

[0030] d) In order to prevent metaled elution, while reducing simultaneously the content of S, P, V, nickel, and Cu among the impurities in a ferritic stainless steel, you have to strengthen a passive-state coat.

[0031] e) If passive-state coating thickness is thickened even if it strengthens a passive-state coat, the contact electricity resistance will increase and cell efficiency will fall remarkably.

[0032] f) In order to strengthen and to suppress metaled elution in a separator environment, without thickening a passive-state coat, it is necessary to make it, as for the content of Cr and Mo, ($\text{Cr}\% + 3 \times \text{Mo}\%$) become 12 - 43% of within the limits.

[0033] g) Although corrosion resistance is secured by adding Mo positively, the influence to the performance of the catalyst currently supported by an anode and the cathode section though Mo is eluted is comparatively slight.

[0034]

[Embodiments of the Invention] The reason for having specified the chemical composition of the separator which consists of a ferritic stainless steel with which the solid-state macromolecule type fuel cell of this invention is equipped hereafter is explained in detail. In addition, % display of the following component shows weight %.

[0035] S: The amount of S in steel needs to consider as 0.005% or less. In S, according to the amount of S in a coexistence-among steel element, and steel, most deposits as a compound nonmetallic inclusion with Mn system sulfide, Cr system sulfide, Fe system sulfide, Ti system sulfides, these compound sulfides, and an oxide. However, in separator environment, any nonmetallic inclusion of composition acts as an origin of the corrosion of a certain thing, and that of the difference of a grade is detrimental to maintenance of passivation, and metaled corrosion elution suppression.

[0036] Moreover, in the situation that the fuel cell is operating, although the inside of the crevice between the separator which consists of a ferritic stainless steel, and MEA (Membrane Electrode Assembly) serves as the situation of pH in a crevice falling and being easy to cause microcell corrosion when a cell reaction and/or oxygen density difference cell corrosion take place, a sulfide system nonmetallic inclusion does the big influence as the corrosion origin in that case, and an acceleration factor. Although the amount of S in steel of the usual mass-production steel exceeds 0.005% and is just over or below 0.008%, in order to prevent the detrimental influence of the above, it is necessary to reduce it to 0.005% or less. The desirable amount of S in steel is 0.002% or less, and the most desirable amount level of S in steel is less than 0.001%, and if it is low, it is as good as a low.

[0037] P: The amount of P in steel needs to be 0.025% or less. The usual stainless steel business steel content level is about 0.026 - 0.035%. P is an unescapable impurity, is located in a line with S, and does the influence of ** in ** to poisoning of an anode and a cathode catalyst bed -- detrimental -- it is base A low is desirable.

[0038] V: V in steel carries out and is required for 0.2% or less. Generally, V is contained as an impurity all over the source of Cr which is an indispensable dissolution raw material at the time of ingoting stainless steel, and a certain amount of mixing is unescapable. However, eluted V does a bad influence not a little to the performance of the catalyst currently supported by an anode and the cathode section. The upper shell of cell property maintenance and a permissible upper limit are 0.2%, and if they are low, they are as good as a low.

[0039] Cu, nickel: Both sides all need to make Cu in steel, and nickel 0.2% or less. Even if it is generally the minute amounts Cu and nickel about an impurity, it has the effect of improving the corrosion resistance of the stainless steel in the low pH environment. However, in a separator environment, since influence is done to poisoning of an anode and a cathode catalyst bed even if it is Cu of the minute amount in a passive-state maintenance state, and nickel ion elution, it is necessary to make an upper limit into 0.2%. Also including mixing from a scrap, although Cu in steel and the amount of nickel have a desirable method of a low, Cu of 0.2% or less of ultralow-volume impurity level and nickel raise the passivation ability of a ferritic stainless steel, and an upper limit is made into 0.2%, in order to also have the operation which suppresses metal elution in the passivation state and to improve a cell performance as a result.

[0040] Both Cr, Mo:Cr, and Mo are basic alloy elements when securing corrosion resistance. so that a content is high -- high -- although it becomes anti-corrosion, there is an inclination to follow on forming high Cr and for ordinary temperature toughness to fall, and if it exceeds 35% in the amount of Cr(s), the production by mass production will become difficult

Moreover, at less than 10.5%, even if it changes other elements, corrosion resistance reservation required as separator becomes difficult.

[0041] Mo is the element made to contain as occasion demands, is little compared with Cr and effective in improving corrosion resistance. The effect of Mo becomes less clear at less than 0.5%. If it is made to contain exceeding 6% when making it contain, deposit evasion of the intermetallic compound of sigma equality is difficult, and since production becomes difficult from the problem of the embrittlement of steel, an upper limit will be made into 5%. Corrosion resistance is secured by carrying out Mo content positively. The influence to the performance of the catalyst currently supported by an anode and the cathode section though Mo is eluted is comparatively slight, and its bad influence is small also to the cation conductivity of a fluorine system ion-exchange-resin film which has a hydrogen ion (proton) exchange group.

[0042] : (Cr%+3Mo%) As stainless steel for separator, it is in the state of passivation in 70 to 100 degrees C [that is the operation temperature of a solid-state macromolecule type fuel cell / at most] environment, and it is required at the time of ** for the contact electricity resistance to be low also-like. It is necessary to suppress an increase and corrosion-product generation in the practical range in passive-state coat thickness. as a requirement for that -- the content of Cr and Mo -- a corrosion index -- it is (Cr%+3Mo%) -- it is required to be in 12 - 43% of within the limits

[0043] The thing which are judged to be appropriate as simulation environment inside the cell in an actual operating state and which is being done for passivation by "pH in 25 degrees C is among 80 degrees C of sulfuric-acid solution of 2.6" is required at least. For that purpose, it is 0.2V vs.S C E in this environment. It is desirable for the passive-state maintenance current density which can be set to be less than two 50microA/cm.

[0044] Si: As for the amount of Si in steel, it is desirable to make it to 0.3% or less. Si is an effective deoxidation element like aluminum in mass-production steel. However, in order that eluted Si may do influence not a little to poisoning of an anode and a cathode catalyst bed, since it is clearly detrimental, the upper shell of cell property maintenance may be 0.3% or less. Although production just over or below 0.25% is the most desirable from a viewpoint of mass-production cost reduction, it is desirable that it is less than 0.2% in separator environment. Less than 0.1% is still more desirable.

[0045] Mn: As for the amount of Mn in steel, considering as 0.4% or less is desirable. Usually, Mn has the operation which fixes S in steel as a sulfide of Mn system, and is effective in improving hot-working nature. Moreover, you may add positively as a deoxidation element or a nickel balance adjustment element. However, although metaled elution advances every only also in the state where the passive state is maintained, if it becomes an amount exceeding 0.4%, eluted Mn ion will do influence not a little to poisoning of an anode and a cathode catalyst bed. Desirably, it is less than 0.1%. If it is 0.45 or less Mn, it can manufacture without also generating problems, such as hot tearing in the case of mass production. A manufacturing-cost rise hardly poses a problem, either.

[0046] C, N: As for C in steel, and N, it is desirable for 0.018% or less and N to be 0.018% or less, and for C to make them 0.025% or less with a value +N% C% from the purpose of an ordinary temperature toughness improvement. C and N are permeated type elements and cause the base material toughness of a high grade ferritic stainless steel, the corrosion resistance of a weld zone, and toughness degradation. Restricting severely becomes the cure against ordinary temperature toughness which poses a problem by the manufacturing process of the hot-rolling coil of a high grade ferritic stainless steel, and C and N can avoid elevation of a manufacturing cost. As C in steel and N are made super-low, since it improves, if ordinary temperature toughness is low, it is as better as a low.

[0047] Ti:Ti is 0.2% or less and is made to contain as occasion demands in the 6 or more times of a value (C-% +N %), and 25 or less times amount of ranges. Since Ti exerts poisoning on an anode and a cathode catalyst bed, although it is originally the element which should be reduced, the minimum amount content is carried out as occasion demands from the viewpoint of the manufacturability reservation by mass production, and processability reservation of sheet metal.

[0048] When weldability is not required, more than value (C-% +N %) x6 time and 10 or less times are the most desirable. When weldability is called for, 10 or more times of a value (C-% +N %) and 16 or less times are the most desirable. In order to avoid board surface crack generating of an inclusion reason, considering as 0.1% or less is desirable. If it is made to contain more than required, it will become the cause of the anode by elution of the metal in a passive-state maintenance state, and cathode catalyst performance degradation.

[0049] Nb:Nb is the element made to contain as occasion demands, and is an alloy element with bonding strength stronger than Cr with the inside C and N of steel like Ti. Nb -- 0.3 -- % -- less than -- it is -- and -- C -- % -- x -- six - C -- % -- x -- 25 -- [- namely, -- Nb -- (-- % --) -- /- C -- (-- % --) -- = -- six - 25 -- % --] -- within the limits -- containing -- making . It is very effective for a toughness improvement including the ordinary temperature toughness of a hot-rolling coil. However, since Nb eluted with corrosion has the evil which deposits on a corrosion side as a corrosion product, and raises the contact electricity resistance, Nb content only from a viewpoint of a base material performance has a desirable method of a low. However, when it is judged that reservation of the performance of a weld zone, and Nb and Ti are made to contain simultaneously, and it is necessary to improve the processability of a cold-rolled-sheet-steel material, the required minimum amount addition is carried out.

[0050] Rare earth elements (rapid eye movement): In a molten steel stage, since bonding strength of rare earth elements with S is very strong, they have the effect which makes S harmless. Therefore, you may add in a form like a misch metal as occasion demands. As for a content, an effect is enough acquired at 0.1% or less.

[0051] You may make elements other than the above-mentioned element contain as occasion demands. For example, it is good for a hot-working nature improvement to make 0.1 or less calcium, Mg, and B contain.

[0052]

[Example] The ferritic stainless steel of 28 sorts of chemical compositions shown in Table 1 was dissolved by 150kg vacuum melting furnace of a high-frequency-induction-heating method. As a dissolution raw material, the raw material with few commercial impurities was selected carefully and used, and the impure amount of resources in steel was adjusted.

[0053]

[Table 1]

| 表1 | | | | | | | | | | | | | | | | | | | (重量%, 残部Fe) | |
|-----|--------|------|------|--------|---------|--------|--------|------|------|------|--------|-------|-------|---------|--------|--------|---------|------------|-------------|--|
| No. | C | Si | Mn | P | S | Cu | Ni | Cr | Mo | Ti | V | N | Al | その他 | C+N | 6(C+N) | 25(C+N) | Cr +3Mo | | |
| 1 | 0.0025 | 0.08 | 0.08 | 0.012 | 0.0008 | 0.006 | 0.003 | 17.6 | 0.82 | 0.10 | 0.007 | 0.005 | 0.012 | | 0.0075 | 0.0450 | 0.1875 | 20.06 | | |
| 2 | 0.0018 | 0.12 | 0.08 | 0.010 | 0.0008 | 0.008 | 0.004 | 18.3 | 0.82 | 0.10 | 0.008 | 0.005 | 0.010 | | 0.0068 | 0.0408 | 0.1700 | 20.76 | | |
| 3 | 0.0019 | 0.16 | 0.06 | 0.011 | 0.0006 | 0.006 | 0.003 | 19.5 | 1.20 | 0.11 | 0.006 | 0.005 | 0.008 | | 0.0069 | 0.0414 | 0.1725 | 23.10 | | |
| 4 | 0.0022 | 0.15 | 0.09 | 0.012 | 0.0009 | 0.005 | 0.005 | 20.5 | 1.81 | 0.10 | 0.008 | 0.006 | 0.011 | | 0.0082 | 0.0492 | 0.2050 | 25.93 | | |
| 5 | 0.0013 | 0.10 | 0.10 | 0.011 | 0.0008 | 0.006 | 0.004 | 25.6 | 0.98 | 0.12 | 0.007 | 0.005 | 0.010 | | 0.0063 | 0.0378 | 0.1575 | 28.54 | | |
| 6 | 0.0020 | 0.08 | 0.08 | 0.012 | 0.0009 | 0.005 | 0.005 | 18.5 | 0.52 | 0.11 | 0.006 | 0.004 | 0.011 | | 0.0060 | 0.0360 | 0.1500 | 20.06 | | |
| 7 | 0.0018 | 0.08 | 0.08 | 0.010 | 0.0006 | 0.005 | 0.005 | 19.2 | 1.82 | 0.11 | 0.008 | 0.006 | 0.012 | | 0.0078 | 0.0468 | 0.1950 | 24.66 | | |
| 8 | 0.0016 | 0.10 | 0.08 | 0.011 | 0.0007 | 0.005 | 0.004 | 19.5 | 2.82 | 0.11 | 0.007 | 0.005 | 0.010 | | 0.0066 | 0.0396 | 0.1650 | 27.96 | | |
| 9 | 0.0012 | 0.09 | 0.10 | 0.012 | 0.0008 | 0.006 | 0.003 | 29.2 | 4.02 | 0.11 | 0.005 | 0.005 | 0.013 | La:0.08 | 0.0062 | 0.0372 | 0.1550 | 41.26 | | |
| 10 | 0.0026 | 0.11 | 0.09 | 0.010 | 0.0008 | 0.013 | 0.003 | 19.2 | 1.88 | 0.10 | 0.008 | 0.005 | 0.012 | | 0.0076 | 0.0456 | 0.1900 | 24.84 | | |
| 11 | 0.0025 | 0.10 | 0.10 | 0.009 | 0.0009 | 0.012 | 0.012 | 19.2 | 2.02 | - | 0.006 | 0.006 | 0.010 | | 0.0085 | 0.0510 | 0.2125 | 25.26 | | |
| 12 | 0.0016 | 0.08 | 0.06 | 0.007 | 0.0007 | 0.012 | 0.015 | 19.0 | 0.82 | - | 0.005 | 0.005 | 0.011 | | 0.0066 | 0.0396 | 0.1650 | 21.46 | | |
| 13 | 0.0015 | 0.08 | 0.08 | 0.006 | 0.0003 | 0.011 | 0.015 | 19.3 | 1.95 | - | 0.008 | 0.005 | 0.012 | | 0.0065 | 0.0390 | 0.1625 | 25.15 | | |
| 14 | 0.0015 | 0.06 | 0.08 | 0.006 | 0.0006 | 0.013 | 0.016 | 18.9 | 2.86 | - | 0.008 | 0.005 | 0.013 | | 0.0065 | 0.0390 | 0.1625 | 27.48 | | |
| 15 | 0.0022 | 0.32 | 0.43 | 0.008 | 0.0005 | 0.010 | 0.012 | 22.3 | 1.82 | - | 0.003 | 0.003 | 0.010 | | 0.0052 | 0.0312 | 0.1300 | 27.76 | | |
| 16 | 0.0025 | 0.08 | 0.08 | 0.007 | 0.0070* | 0.010 | 0.011 | 16.8 | * | - | 0.120 | 0.008 | 0.010 | | 0.0105 | 0.0630 | 0.2625 | 16.80 | | |
| 17 | 0.0022 | 0.28 | 0.09 | 0.007 | 0.0075* | 0.010 | 0.008 | 16.5 | - | - | 0.120 | 0.007 | 0.009 | | 0.0092 | 0.0552 | 0.2300 | 16.50 | | |
| 18 | 0.0020 | 0.06 | 0.45 | 0.008 | 0.0065* | 0.009 | 0.009 | 16.8 | - | - | 0.110 | 0.007 | 0.010 | | 0.0090 | 0.0540 | 0.2250 | 16.80 | | |
| 19 | 0.0016 | 0.06 | 0.07 | 0.029* | 0.0068* | 0.010 | 0.010 | 16.8 | - | - | 0.130 | 0.006 | 0.008 | | 0.0076 | 0.0456 | 0.1900 | 16.80 | | |
| 20 | 0.0015 | 0.30 | 0.45 | 0.028* | 0.0065* | 0.150 | 0.120 | 16.7 | - | - | 0.110 | 0.007 | 0.010 | | 0.0085 | 0.0510 | 0.2125 | 16.70 | | |
| 21 | 0.0038 | 0.05 | 0.08 | 0.007 | 0.0058* | 0.750* | - | 19.2 | - | - | 0.110 | 0.005 | 0.008 | | 0.0088 | 0.0528 | 0.2200 | 19.20 | | |
| 22 | 0.0041 | 0.06 | 0.08 | 0.008 | 0.0065* | - | 0.152 | 19.0 | - | - | 0.110 | 0.006 | 0.009 | | 0.0101 | 0.0606 | 0.2525 | 19.0 | | |
| 23 | 0.0200 | 0.05 | 0.06 | 0.006 | 0.0072* | - | - | 19.2 | 1.80 | - | 0.120 | 0.009 | 0.018 | | 0.0290 | 0.1740 | 0.7250 | 24.6 | | |
| 24 | 0.0250 | 0.45 | 0.50 | 0.028* | 0.0085* | 0.120 | 0.080 | 11.5 | 0.02 | * | 0.110 | 0.020 | 0.002 | Nb:0.48 | 0.0450 | 0.2700 | 1.1250 | 11.56 | | |
| 25 | 0.0280 | 0.25 | 0.45 | 0.030* | 0.0075* | 0.120 | 0.100 | 16.8 | 0.02 | * | 0.250* | 0.023 | 0.003 | | 0.0510 | 0.3060 | 1.2750 | 16.86 | | |
| 26 | 0.0580 | 0.34 | 1.20 | 0.030* | 0.0061* | 0.230* | 8.210* | 18.5 | 0.08 | * | 0.080 | 0.031 | 0.002 | | 0.0890 | 0.5340 | 2.2250 | 18.74 | | |
| 27 | 0.0130 | 0.62 | 1.00 | 0.028* | 0.0062* | 0.240* | 12.30* | 17.5 | 2.24 | * | 0.070 | 0.023 | 0.003 | | 0.036 | 0.2160 | 0.9000 | 24.22 | | |
| 28 | " | " | " | " | " | " | " | " | " | * | " | " | " | | " | " | " | 24.22 | | |
| 29 | 0.0230 | 0.24 | 0.53 | 0.025 | 0.0230 | 0.080 | 0.020 | 10.1 | - | - | 0.030 | 0.005 | 0.002 | | 0.028 | 0.168 | 0.7000 | 10.10 | | |

* 本発明で規定する範囲外を示す

[0054] After heating in the atmosphere the ingot of a round shape [cross section / which carried out ingot making] at 1230

degrees C for 3 hours, hot forging of it was carried out with the press method forging machine, and it made the slab for an examination of the two following sorts of sizes to each ingot.

[0055] ** The slab of the thickness of 30mm, width of face of 100mm, the length [of 120mm] ** thickness of 70mm, width of face of 380mm, and length [of 550mm] ** was hot-rolled, was used as the hot rolled sheet steel with a thickness of 6mm, and was annealed on the heat insulator winding conditions which subsequently simulated the temperature history immediately after the hot-rolling end by mass production. In order to investigate the hot-rolling coil toughness in ordinary temperature, the Charpy impact test was presented. The test piece was made into JIS Z2202 No. 4 half size.

** Slab carried out cutting of the slab front face with machining, removed the surface scale, and made slab with a thickness of 62mm to it. After heating and hot-rolling this slab at 1200 degrees C in the atmosphere and making 4mm in thickness, it cooled slowly like ** on the heat insulator winding conditions which simulated the temperature history immediately after the hot-rolling end by mass production.

[0056] According to the chemical composition, forced-air cooling of the solution treatment for maintenance 4 minutes was performed and carried out to this hot rolled sheet steel at the following temperature.

** The hot rolled sheet steel of No.25 of Table 1 830 degrees C ** No.11-15 of Table 1, hot rolled sheet steel of 16-23 The hot rolled sheet steel of No.1-10 of the 900 degree-C ** table 1 No. of the 930-degree-C ** table 1 -- hot rolled sheet steel of 24 and 29 No. of the 980 degree-C ** table 1 -- hot rolled sheet steel of 26 and 27 recrystallization advanced and 1080 degree-C each temperature was made into the temperature to which an intermetallic compound dissolves In-furnace time was about 20 minutes.

[0057] Subsequently, inserting intermediate annealing on the way using a multi-stage formula ZENJIMA forming-roll rolling mill, it cold-rolled and 0.3mm in thickness was made to the hot rolled sheet steel which carried out solution treatment. Performing the last finishing annealing in the bright-annealing furnace of hydrogen atmosphere whose dew-point is -50 degrees C or less, temperature presupposed that it is the same as the annealing temperature of a hot rolling material. The holding time was 1 minute and was about 3 minutes at in-furnace time.

[0058] The separator for the charge to the test piece for evaluating the passive-state coat in the separator simulation environment of the following size and an actual solid-state macromolecule type fuel cell from this cold rolling annealed material was manufactured by press forming.

[0059] In addition, about No.27 of the example of comparison, 5 micrometer thickness of one side was plated with gold after producing the test piece for simulation environment, and separator.

[0060] The test piece for simulation environment : 0.3mm in the thickness of 0.3mm, width of face of 10mm, length 10mm separator:thickness 80mm long, 80mm gas passageway wide : Shot polish finishing of these front faces is mechanically carried out using the SiC abrasive grain for shot processing the interval of 1.2mm (corrugated processing) of a height of 0.8mm, a mountain, and a mountain. Ultrasonic cleaning for 15 minutes is performed in 5%HNO₃+3%HF and 40 degrees C. Furthermore, each examination was presented, after having performed alkali spraying degreasing processing in which sodium-hydroxide solution was used 6%, and the stream's having performed distilled water soak cleaning 3 times in the batch type tank after simple rinsing, performing distilled water spraying washing for 4 minutes further and carrying out cold blast Dreier dryness just before an examination.

[0061] While carrying out the temperature up of the sulfuric-acid solution whose pH in 25 degrees C adjusted using the sulfuric acid of reagent chemicals as an examination in simulation environment is 2.6 to 80 degrees C, immersing a test piece into the solution for 6 hours and evaluating the existence of passivation from color change of a corrosion weight loss, hydrogen gassing from a material front face, and a testing liquid, in order to investigate a metaled elution grade to accuracy more, it is 0.2Vvs S C E. The passive-state holding current density which can be set was measured.

[0062] The Charpy-impact-test result and the test result in separator simulation environment were as being shown in Table 2.

[0063]

[Table 2]

表2

| No | 25℃におけるpHが2.6である 硫酸水溶液80℃での評価 | | 固体電解質型燃料電池セル 装填による評価 | | 圧延後空冷した熱延鋼板 の常温 (25℃) での衝撃値 (試験片: JIS-4号H-7サイズ (kgf-m/cm ²)) | 備考 |
|----|----------------------------------|----------------------------------------------------------------|-----------------------------------------|--|---------------------------------------------------------------------------------------|------|
| | 不働態化 の有無 | 0.2V vs. SCEにおける 不働態保持電流密度 ($\mu\text{A}/\text{cm}^2$) | 1時間経過後の単セル電圧 低下率 1-(経過後電圧V/初期電圧V) | | | |
| 1 | 有り | 10 ~ 20 | <0.05 | | >15 | 本発明例 |
| 2 | " | 20 ~ 30 | <0.05 | | >15 | |
| 3 | " | 10 ~ 20 | <0.05 | | >15 | |
| 4 | " | 10 ~ 20 | <0.05 | | >15 | |
| 5 | " | 10 ~ 20 | <0.05 | | >15 | |
| 6 | " | 10 ~ 20 | <0.05 | | >15 | |
| 7 | " | <10 | <0.05 | | >15 | |
| 8 | " | <10 | <0.05 | | >15 | |
| 9 | " | <10 | <0.05 | | >15 | |
| 10 | " | 10 ~ 20 | <0.05 | | >15 | |
| 11 | " | 10 ~ 20 | <0.05 | | >15 | |
| 12 | " | <10 | <0.05 | | >15 | |
| 13 | " | <10 | <0.05 | | >15 | |
| 14 | " | <10 | <0.05 | | >15 | |
| 15 | " | <10 | <0.05 | | >15 | |
| 16 | 無し | 50 ~ 70 | 0.3 ~ 0.5 | | 2 | 比較例 |
| 17 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 2 | |
| 18 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 3 | |
| 19 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 2 | |
| 20 | " | 50 ~ 70 | 0.3 ~ 0.8 | | 2 | |
| 21 | 有り | 50 ~ 70 | 0.3 ~ 0.5 | | 3 | |
| 22 | " | 50 ~ 70 | 0.3 ~ 0.5 | | 3 | |
| 23 | " | 50 ~ 70 | 0.5 ~ 0.7 | | 1 | |
| 24 | " | >1mA/cm ² | >0.8 | | 12 | |
| 25 | " | 50 ~ 70 | >0.8 | | 12 | |
| 26 | " | 10 ~ 20 | >0.8 | | 25 | |
| 27 | " | 10 ~ 20 | >0.8 | | 28 | |
| 28 | " | <10 | <0.05 | | 28 | |
| 29 | " | >1mA/cm ² | >0.8 | | 18 | |

[0064] In the example of this invention, it is in a passivation state in the sulfuric-acid solution whose pH in 25 degrees C which carried out the temperature up to 80 degrees C is 2.6, and the "passive-state holding current density" which shows the grade of elution has become two or less 20microA/cm so that clearly from Table 2.

[0065] In case stainless steel is applied as separator for solid-state macromolecule type fuel cells, passive-state holding current density cannot be overemphasized by that it is desirable to consider as low level as much as possible. It is important for it to be stabilized and to take a low value, less than two 10microA/cm is the most desirable, and it is desirable that it is subsequently 10-20microA/cm2.

[0066] The passive-state current density of the example of comparison shows that it is 30-80microA/cm2, and it is in the state where comparatively big elution has taken place from separator although it can say that it is suppressed.

[0067] This invention persons are a relation with the performance characteristic in a system single cell cell to passive-state holding current density >50microA/cm2 as criteria which judge the application propriety as a separator material for fuel cells. It was judged that a performance was inadequate then. Passive-state holding current density sets into two or less 50microA/cm material. A **** cell evaluation examination did not come to check the-like performance degradation at the time of ** of the grade which poses a problem, either, and is judged to be very suitable as quick simulation environment-assessment conditions. Also in this result, in the case of the example of invention, it is the same level as the gilding material (sample offering steel 27) which is one of the most desirable metal materials in solid-state macromolecule type fuel cell environment, and it was judged that it sees relatively and can secure a good performance.

[0068] Next, as characterization in the state where the interior of an actual solid-state macromolecule type single cell cell was loaded as separator, after passing fuel gas in the cell, the voltage of a single cell cell was measured after 1-hour progress, and the decreasing rate of voltage was investigated by comparing with early voltage. In addition, it asked for the decreasing rate by 1- (voltage V / initial voltage v after 1-hour progress).

[0069] The marketing cell cell FC50 made from U.S. Electrochem was converted and used for the solid-state macromolecule type fuel single cell cell used for evaluation.

[0070] As cathode pole side gas, air was used 99.9999%, using hydrogen gas as gas for anode pole side fuel. Based on the exhaust gas moisture density measurement by the side of cell appearance, the main part of a cell is an entering side, and adjusted the humidity control inside a cell while it kept the whole warm at 78**2 degrees C. The pressure inside a cell is one

atmospheric pressure. Hydrogen gas and the introductory gas pressure to the cell of air were adjusted by 0.04-0.20bar. The cell performance evaluation measured-like [state / where 500 mA/cm²-0.62V have been checked on single cell voltage] at the time of **.

[0071] As a system for single cell performance measurements, it is 890 made from U.S. scree BUNA. The fuel cell instrumentation system based on series was converted and used. Although it is expected according to cell operational status that a property has change, it is the comparative evaluation in the same conditions.

[0072] The result was shown in Table 2.

[0073] In the example of this invention, all the rates of sag are 0.05 or less, and became No.27 are expensive and equivalent to the separator which high corrosion resistance plated with gold so that clearly from Table 2. Moreover, in the example of comparison which separated from the chemical composition specified by this invention, the rate of sag was very as large as 0.3-0.8.

[0074] The prolonged examination was carried out with some test pieces, and the short-time-test result which evaluation ***** showed in Table 2, and the approximated correlative result were obtained.

[0075] Generally the toughness in the ordinary temperature of stainless steel is inferior in the ferritic stainless steel compared with the austenitic stainless steel. however, when C and N content are the examples of this invention of a low series compared with the case where C in steel and N content are the high examples of comparison so that clearly from the Charpy-test result of Table 2, it has the toughness which was markedly alike and was excellent Generally, since it will be seemingly improved if board thickness becomes thin, if ordinary temperature toughness is the level in the case of being this invention, it will completely be satisfactory practically. That is, it can be said that the ordinary temperature toughness of the hot-rolling coil which poses a problem at the time of high grade ferritic-stainless-steel manufacture is good. Generally, since it will be seemingly improved if board thickness becomes thin, if ordinary temperature toughness is the level of the steel of this invention, it will completely be satisfactory [toughness] practically.

[0076]

[Effect of the Invention] Since separator does not need to consist of a ferritic stainless steel and the solid-state macromolecule type fuel cell of this invention does not need to give expensive gilding, it can do manufacture cheaply.

[Translation done.]

WEST

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Oct 10, 2000

DERWENT-ACC-NO: 2000-674536

DERWENT-WEEK: 200108

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TITLE: Solid state polymeric type fuel battery for motor vehicle has separator consisting of ferritic stainless steel containing specified amount of alloying element composition, interposed between unit batteries

PATENT-ASSIGNEE:

ASSIGNEE

CODE

SUMITOMO METAL IND LTD

SUMQ

PRIORITY-DATA: 1999JP-0103357 (April 9, 1999)

PATENT-FAMILY:

| PUB-NO | PUB-DATE | LANGUAGE | PAGES | MAIN-IPC |
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| JP 3097690 B1 | October 10, 2000 | | 009 | H01M008/02 |
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INT-CL (IPC): C22 C 38/00; C22 C 38/46; C22 C 38/50; H01 M 8/02; H01 M 8/10

ABSTRACTED-PUB-NO: JP 3097690B

BASIC-ABSTRACT:

NOVELTY - A solid state polymeric type fuel battery (1) has separators consisting of ferritic stainless steel interposed between unit batteries. Stainless steel comprises (in weight%) S (0.005% or less), P (0.025% or less), Va (0.2% or less), Ni (0.2% or less), Cu (0.2% or less), Cr (10.5-35%), Mo (0-6%), Si (0.3% or less), Mn (0.4% or less), C (0.018% or less), N (0.018% or less) and rare earth elements (0-0.1%).

DETAILED DESCRIPTION - The solid state polymeric type fuel battery (1) consists of separators (5a,5b) interposed between unit batteries. The unit battery is a laminate of central solid polymeric electrolyte film (2), fuel electrode film (3) and oxidizing agent electrode film (4). The fuel gas and oxidizing gas are supplied to multilayered fuel battery so that the battery generates DC electric power. The total content of carbon and nitrogen in battery is 0.025% or less. The value of (Cr+3Mo) in separator is 10.5-43%.

USE - As small sized distributed power supplier for motor vehicles and domestic use.

ADVANTAGE - Since expensive gilding is not needed, the manufacture of fuel battery is inexpensive and poisoning of each supported electrode in the fuel battery is minimized.

DESCRIPTION OF DRAWING(S) - The figure shows the drawing of the solid state

polymeric type fuel battery.

Fuel battery 1

Solid state electrolytic film 2

Fuel electrode film 3

Oxidizing agent electrode film 4

Separators 5a,5b

CHOSEN-DRAWING: Dwg.1/1

TITLE-TERMS: SOLID STATE POLYMERISE TYPE FUEL BATTERY MOTOR VEHICLE SEPARATE CONSIST
FERRITE STAINLESS STEEL CONTAIN SPECIFIED AMOUNT ALLOY ELEMENT COMPOSITION
INTERPOSED UNIT BATTERY

DERWENT-CLASS: A85 L03 M27

CPI-CODES: A11-B09A2; A12-E06B; L03-E04; M27-A04; M27-A04C;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1] 018 ; P0000 Polymer Index [1.2] 018 ; ND01 ; Q9999 Q7341 Q7330 ;
Q9999 Q8764

SECONDARY-ACC-NO:

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